Pathways to the Oxidation of Copper

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Motivation and Accomplishments

Understanding oxidation leads to a better control of:

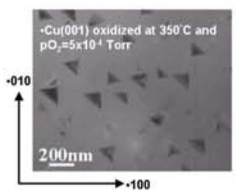
- Corrosion
- Heterogeneous catalysis
- Growth of oxide layers for devices
- Performance of nanoscale materials

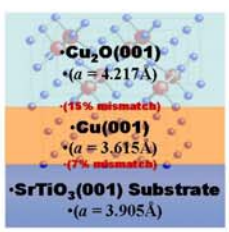
Our studies of Cu(001) oxidation:

- Find c(2x2) structure over a wide of (pO_2, T)
- Explain conflicting results in the literature
- Demonstrate that latency is connected with saturation of this reconstruction

Background Information

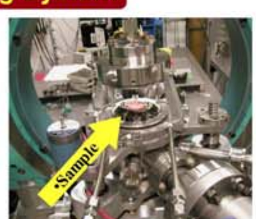
- Initial formation of oxide is through islands
- Oxygen induces a reconstruction of the Cu (001) surface, usually $2\sqrt{2} \times \sqrt{2}R45°$
- Theory predicts sub-surface oxygen plays an important role
- Impurities create problems but can be minimized by thin film growth
- We produce epitaxial films on $SrTiO_3$ substrates by ex-situ evaporation under UHV conditions
- Oxide formation is studied using *in situ* x-ray scattering under quasi-equilibrium conditions

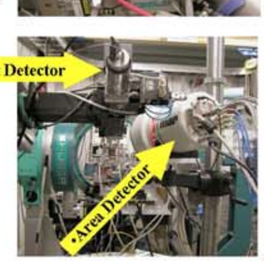




Materials Processing System

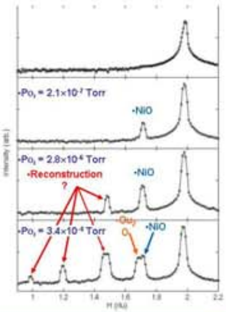
- Precisely controlled atmosphere (Ar, O_2, CO, CO_2, H_2) with base pressure <10^{-7} Torr
- Temperatures between RT and 1000°C
- Two stage residual gas analysis
- Mounts on standard diffractometer





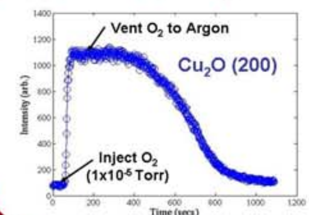
Future Directions

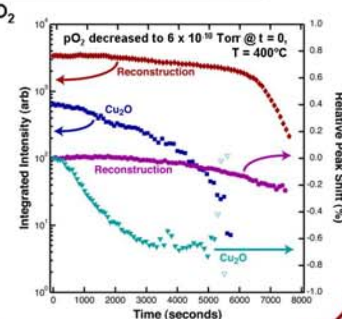
- Alloying causes more complex oxidation behavior (e.g. oxidation of Cu-Ni alloys is very different than that of pure Cu)
- Studies are also being extended to oxide-supported metal and alloy islands (relevant to redox catalysis)
- X-ray scattering studies will be complemented by theory and *in situ* TEM, ESEM, and spectroscopy



Oxidation and Reduction are Reversible

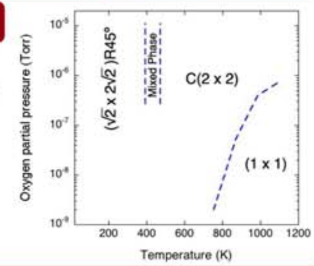
Cu_2O can be fully reduced by lower PO_2 (below). The c(2x2) reconstruction (right) persists until Cu_2O is gone (oxide phase supplies O_2)



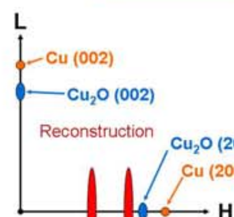


Surface Phase Diagram

- Found an ordered surface structure with c(2x2) symmetry
- c(2x2) is stable over a wide range of T and pO_2 (resolved literature controversy).
- Does surface structure modify oxidation behavior?

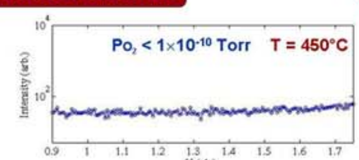


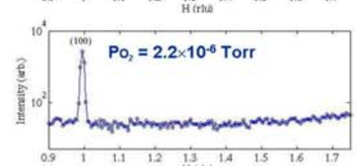
In Situ X-Ray Measurements

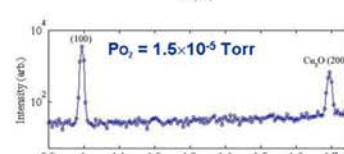


While varying Po_2, monitor:

- Adsorption (CTRs)
- Cu strain state (●)
- Surface reconstructions (●)
- Cu_2O nucleation & growth (●)
- Cu-Cu_2O phase equilibria (intensity of ● increase or decrease?)







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